We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

6

Fourier Transformation Method for Computing NMR Integrals over Exponential Type Functions

Hassan Safouhi
Mathematical Section, Campus Saint-Jean,
University of Alberta, Alberta
Canada

1. Introduction

Experimental methods based on magnetic resonance are among the most used techniques for investigating molecular and electronic structure. Nuclear magnetic resonance (NMR) is mostly applied to closed-shell molecules and can be used for structural research of matter in solid, liquid and gaseous form. The computation of NMR parameters, which are of a great interest not only in chemistry but also in biology and solid-state physics, presents severe analytical and numerical difficulties [Dickson & Ziegler (1996); Ditchfield (1974); Fukui et al. (2004); Helgaker et al. (1999); Ishida (2003); London (1937); Pople et al. (1968); Pyykkö (1988); Schreckenbach & Ziegler (1995); Vaara (2007); Watson et al. (2004)]. The computation of NMR parameters for any of the standard models of quantum chemistry constitute an important challenge [Helgaker et al. (1999)]. Calculations involving a magnetic field should preserve gauge invariance. This is conveniently accomplished by using a gauge including atomic orbitals (GIAO) [London (1937)], which is based on atom-centered basis functions with an explicit field dependence. Magnetic properties are sensitive to the quality of the basis sets due to many contributing physical phenomena arising from both the vicinity of the nucleus and from the valence region. A good atomic orbital basis should decay exponentially for large distances [Agmon (1985)] and should also satisfy Kato's conditions for exact solutions of the appropriate Schrödinger equation [Kato (1957)]. Exponential type functions (ETFs) are better suited than Gaussian functions (GTFs) [Boys (1950a;b)] to represent electron wave functions near the nucleus and at long range. Among the ETFs, Slater type functions (STFs) [Slater (1932)], have a dominating position due to their simple analytic expression, but their multi-center integrals are extremely difficult to evaluate for polyatomic molecules, particularly bi-electronic terms. We note that many researchers hope that the next generation of ab initio programs will be based on the usage of ETFs. Indeed much effort is being made to develop efficient molecular algorithms for integrals over conventional ETFs (STFs or B functions) [Barnett (1990); Fernández et al. (2001); Kutzelnigg (1988); Niehaus et al. (2008); Ozdogan & (Editors); Rico et al. (1998; 1999; 2001); Steinborn et al. (2000); Weatherford & Jones (1982)].

Various studies focussed on the use of B functions. The use of B functions was proposed by Shavitt [Shavitt (1963)], since reduced Bessel functions possess a representation in terms of a remarkably simple Gauss transform. Detailed discussions of the mathematical properties of

reduced Bessel functions and of their anisotropic generalizations can be found in [Weniger (1982)]. Furthermore, B functions have much more appealing properties applicable to multi-center integral problems, compared to other exponentially decaying functions [Filter & Steinborn (1978a;b); Steinborn & Filter (1975); Weniger (2005); Weniger & Steinborn (1983a)]. The multi-center molecular integrals over B functions can be computed much more easily than the corresponding integrals of other exponentially decaying functions. This can be explained in terms of the Fourier transform of B functions, which is of exceptional simplicity among exponentially decaying functions [Niukkanen (1984); Weniger (1982); Weniger & Steinborn (1983b)]. Moreover, the Fourier transforms of STFs, of hydrogen eigenfunctions, or of other functions based on the generalized Laguerre polynomials can all be expressed as finite linear combinations of Fourier transforms of B functions [Weniger (1985); Weniger & Steinborn (1983b)]. The basis set of B functions is well adapted to the Fourier transform method [Geller (1962); Grotendorst & Steinborn (1988); Prosser & Blanchard (1962); Trivedi & Steinborn (1983)], which allowed analytic expressions to be developed for molecular multi-center integrals over B functions [Grotendorst & Steinborn (1988); Trivedi & Steinborn (1983)].

Of the NMR parameters, the nuclear shielding tensor is of a great importance. The computation of the shielding tensor presents severe analytical and numerical difficulties especially when using ETFs as a basis set of atomic orbitals. The main difficulty arises from the operators associated with these parameters. An example of such operators is $3\,r_{jN,\beta}\left(\vec{r}_{jN}\cdot\vec{\sigma}(j)\right)/r_{jN}^{5}$, where β represents a cartesian coordinates, $\vec{r}_{jN}$ is the vector separating the j^{th} electron and the N^{th} nuclei and σ stands for Pauli spin matrix. These operators lead to extremely complicated integrals. Analytic treatment of the NMR parameters over GTFs was a subject of many articles (see for example [Ishida (2003)] and references therein). Although, the interest of using ETFs in the computation of NMR parameters is increasing [see the pioneer work by Dickson & Ziegler (1996); Schreckenbach & Ziegler (1995)] and Watson et al. (2004)], no effort was dedicated to their analytic treatment over ETFs. Straightforward numerical integration was used for the computation of integrals associated with these parameters.

The analytical development of NMR integrals can be obtained using the Fourier transform method combined with B functions as a basis set of atomic orbitals [Berlu & Safouhi (2008); Safouhi (2010b); Slevinsky et al. (2010)]. The obtained analytic expressions turned out to be similar to those obtained for the so-called three-center nuclear attraction integrals (zeroth order integrals). The latter were the subject of significant research [Berlu & Safouhi (2003); Duret & Safouhi (2007); Fernández et al. (2001); Grotendorst & Steinborn (1988); Homeier & Steinborn (1993); Niehaus et al. (2008); Rico et al. (1998; 1999); Safouhi (2001b; 2004); Slevinsky & Safouhi (2009)]. In our research, we used techniques based on extrapolation methods combined with numerical quadratures to compute the analytic expressions of the NMR integrals. Numerical tables are listed and we refer the interested reader to [Safouhi (2010b); Slevinsky et al. (2010)] for an extensive list of numerical tables as well as detailed numerical discussions.

2. Molecular integrals in the absence of magnetic fields

In the absence of magnetic fields, the molecular electronic Hamiltonian operator $\mathcal{H}_{\text{e}}$ corresponding to total energy E_{e} for a molecule of N nuclei and n_e electron is given by:

$$\mathcal{H}_{\mathrm{e}} = -\frac{1}{2}\sum_{j=1}^{n_e}\nabla_j^2 - \sum_{j=1}^{n_e}\sum_{K=1}^{N}\frac{Z_K}{r_{jK}} + \sum_{i=1}^{n_e}\sum_{j>i}\frac{1}{r_{ij}}, \tag{1}$$

where:

- Z_K is the atomic number of the K^{th} nucleus whose mass is M_K.
- r_{jK} is the distance that separates the K^{th} nucleus from the j^{th} electron.
- r_{ij} is the distance that separates the i^{th} electron from the j^{th} electron.
- ∇_j^2 is the Laplacian operators for the coordinates of electron j.

The stationary Schrödinger equation that needs to be solved is:

$$\mathcal{H}_{\mathrm{e}}\,\Psi(\boldsymbol{r},\boldsymbol{R}) \;=\; E_e\,\Psi(\boldsymbol{r},\boldsymbol{R}).$$

The above Schrödinger equation is solved only in the case of hydrogen-like atom. The solutions are one-electron functions and are referred to as hydrogen-like atomic orbitals. These atomic orbitals form a complete and orthonormal basis. The use of hydrogen-like atomic orbitals was prevented due to the fact that their molecular multi-center integrals are extremely difficult to evaluate analytically and numerically. Linear combinations of the hydrogen-like atomic orbitals lead to STFs, which form the most popular basis set of atomic orbitals. Unormalized STFs are given by [Slater (1932)]:

$$\chi_{n,l}^{m}(\zeta,\vec{r}) \;=\; r^{n-1}\,\mathrm{e}^{-\zeta\,r}\,Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{2}$$

where $Y_l^m(\theta,\varphi)$ is the surface spherical harmonic [Condon & Shortley (1951)] and where n is the principal quantum number, l is the orbital angular momentum number and m is the magnetic quantum number.

The B functions are given by [Filter & Steinborn (1978a); Steinborn & Filter (1975)]:

$$B_{n,l}^{m}(\zeta,\vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!}\,\hat{k}_{n-\frac{1}{2}}(\zeta r)\,Y_l^m(\theta_{\vec{r}},\varphi_{\vec{r}}), \tag{3}$$

where $\hat{k}_{n-\frac{1}{2}}(\zeta\,r)$ stands for the reduced spherical Bessel function of the second kind [Shavitt (1963); Steinborn & Filter (1975)]:

$$\hat{k}_{n+\frac{1}{2}}(z) = z^n\,e^{-z}\sum_{j=0}^{n}\frac{(n+j)!}{j!\,(n-j)!}\,\frac{1}{(2\,z)^j}. \tag{4}$$

STFs can be expressed as finite linear combinations of B functions [Filter & Steinborn (1978a)]:

$$\chi_{n,l}^{m}(\zeta,\vec{r}) \;=\; \frac{1}{\zeta^{n-1}}\sum_{p=\tilde{p}}^{n-l}\frac{(-1)^{n-l-p}\;2^{2p+2l-n}\;(l+p)!}{(2p-n+l)!\;(n-l-p)!}\,B_{p,l}^{m}(\zeta,\vec{r}), \tag{5}$$

where $\tilde{p} = \dfrac{n-l}{2}$ if $n-l$ is even or $\tilde{p} = \dfrac{n-l+1}{2}$ if $n-l$ is odd.

2.1 Fourier transform in molecular multi-center integrals calculation

The Fourier transform of B functions, which is of exceptional simplicity among exponentially decaying functions, is given by [Niukkanen (1984); Weniger (1982); Weniger & Steinborn (1983b)]:

$$\bar{B}^{m}_{n,l}(\zeta,\vec{p}) \;=\; \sqrt{\frac{2}{\pi}}\,\zeta^{2n+l-1}\,\frac{(-i\,|p|)^{l}}{(\zeta^{2}+|p|^{2})^{n+l+1}}\,Y^{m}_{l}(\theta_{\vec{p}},\varphi_{\vec{p}}). \tag{6}$$

In [Trivedi & Steinborn (1983)], the Fourier transform method is used in combination with equation (6) to derive analytic expressions for the following integrals:

$$\mathcal{T}=\int_{\vec{r}}\left[B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right]^{*}\,e^{-i\,\vec{k}\,\cdot\,\vec{r}}\,B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}-\vec{R}_2)\,\mathrm{d}\vec{r}. \tag{7}$$

The main idea of the Fourier integral transformation is given by:

$$\begin{aligned}\int[f(\vec{r})]^{*}\,e^{-i\vec{x}.\vec{r}}\,g(\vec{r}-\vec{R})\,\mathrm{d}\vec{r} &= (2\pi)^{-3/2}\int\left[\int\left[\bar{f}(\vec{q})\right]^{*}\,e^{-i\vec{q}.\vec{r}}\,e^{-i\vec{x}.\vec{r}}\,g(\vec{r}-\vec{R})\,\mathrm{d}\vec{q}\right]\,\mathrm{d}\vec{r}\\ &= e^{-i\vec{x}.\vec{R}}\int\left[\bar{f}(\vec{q})\right]^{*}\,e^{-i\vec{q}.\vec{R}}\,(2\pi)^{-3/2}\left[\int e^{-i(\vec{q}+\vec{x}).(\vec{r}-\vec{R})}\,g(\vec{r}-\vec{R})\,\mathrm{d}\vec{r}\right]\,\mathrm{d}\vec{q}\\ &= e^{-i\vec{x}.\vec{R}}\int\bar{f}^{*}(\vec{q})\,e^{-i\vec{q}.\vec{R}}\,\bar{g}(\vec{q}+\vec{x})\,\mathrm{d}\vec{q},\end{aligned} \tag{8}$$

where $\bar{f}(\vec{k})$ stands for the Fourier transform of $f(\vec{r})$. The function $f(\vec{r})$ and its Fourier transform $\bar{f}(\vec{k})$ are connected by the symmetric relationships:

$$\bar{f}(\vec{k})=(2\pi)^{-3/2}\int_{\vec{r}}e^{-i\vec{k}\cdot\vec{r}}\,f(\vec{r})\,\mathrm{d}\vec{r}\qquad\text{and}\qquad f(\vec{r})=(2\pi)^{-3/2}\int_{\vec{k}}e^{\,i\vec{k}\cdot\vec{r}}\,\bar{f}(\vec{k})\,\mathrm{d}\vec{k}. \tag{9}$$

Replacing f by $B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})$ and g by $B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}-\vec{R})$ we obtain:

$$\int\left[B^{m_1}_{n_1,l_1}(\zeta_1,\vec{r})\right]^{*}\,e^{-i\vec{x}.\vec{r}}\,B^{m_2}_{n_2,l_2}(\zeta_2,\vec{r}-\vec{R})\,\mathrm{d}\vec{r}=e^{-i\vec{x}.\vec{R}}\int\left[\bar{B}^{m_1}_{n_1,l_1}(\zeta_1,\vec{q})\right]^{*}\,e^{-i\vec{q}.\vec{R}}\,\bar{B}^{m_2}_{n_2,l_2}(\zeta_2,\vec{q}+\vec{x})\,\mathrm{d}\vec{q}. \tag{10}$$

Equations (10) and (6) led to an analytic expression for the integral $\mathcal{T}$ in equation (7). This analytic expression is given by [Trivedi & Steinborn (1983)]:

$$\begin{aligned}\mathcal{T} = {}& \frac{(4\pi)^{3}\,(2l_1+1)!!\,(2l_2+1)!!\,(n_1+l_1+n_2+l_2+1)!\,\zeta_1^{2n_1+l_1-1}\,\zeta_2^{2n_2+l_2-1}}{(n_1+l_1)!\,(n_2+l_2)!\,2^{n_1+n_2+l_1+l_2+1}}\\ &\times\sum_{l_1'=0}^{l_1}(-i)^{l_1+l_1'}\sum_{m_1'=-l_1'}^{l_1'}\frac{\langle l_1m_1\,|l_1'm_1'|\,l_1-l_1'm_1-m_1'\rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!}\\ &\times\sum_{l_2'=0}^{l_2}(-i)^{l_2+l_2'}\sum_{m_2'=-l_2'}^{l_2'}\frac{\langle l_2m_2\,|l_2'm_2'|\,l_2-l_2'm_2-m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!}\\ &\times\sum_{l'=l'_{\min},2}^{l_1'+l_2'}(-1)^{l_1'}\,\langle l_2'm_2'\,|l_1'm_1'|\,l'm_2'-m_1'\rangle\;R_2^{l'}\,Y_{l'}^{m_2'-m_1'}(\theta_{\vec{R}_2},\varphi_{\vec{R}_2})\\ &\times\sum_{l_{12}=l_{12min},2}^{l_1-l_1'+l_2-l_2'}\langle l_2-l_2'm_2-m_2'\,|l_1-l_1'm_1-m_1'|\,l_{12}m_{12}\rangle\;Y_{l_{12}}^{m_{12}}(\theta_{\vec{k}},\varphi_{\vec{k}})\end{aligned}$$

$$\times \sum_{j=0}^{\Delta l} \frac{(-2)^j \binom{\Delta l}{j}}{(n_1+n_2+l_1+l_2-j+1)!}$$
$$\times \int_{s=0}^{1} s^{n_{22}} (1-s)^{n_{11}} k^{l_1-l_1'+l_2-l_2'} \frac{\hat{k}_\nu [R_2 \gamma(s,k)]}{[\gamma(s,k)]^{n_\gamma}} e^{-i(1-s)\vec{k}\cdot\vec{R}_2} \mathrm{d}s, \quad (11)$$

where:

$$\begin{aligned} n_\gamma &= 2(n_1+n_2+l_1+l_2)-(l_1'+l_2'+l')+1 \\ \gamma(s,k) &= \sqrt{(1-s)\zeta_1^2+s\zeta_2^2+s(1-s)k^2} \\ \nu &= n_1+n_2+l_1+l_2-l'-j+\tfrac{1}{2} \\ m_{12} &= (m_2-m_2')-(m_1-m_1') \\ n_{11} &= n_1+l_1+l_2-l_2' \\ n_{22} &= n_2+l_2+l_1-l_1' \\ \Delta l &= \tfrac{l_1'+l_2'-l'}{2}, \end{aligned} \quad (12)$$

Gaunt coefficients $\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle$ are defined by [Gaunt (1929)]:

$$\langle l_1 m_1 | l_2 m_2 | l_3 m_3 \rangle = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} [Y_{l_1}^{m_1}(\theta,\varphi)]^* Y_{l_2}^{m_2}(\theta,\varphi) Y_{l_3}^{m_3}(\theta,\varphi) \sin(\theta) \, \mathrm{d}\theta \, \mathrm{d}\varphi. \quad (13)$$

Equation (11) led to analytical expressions for all molecular multi-center integrals over B functions or STFs [Grotendorst & Steinborn (1988); Safouhi (2001a); Trivedi & Steinborn (1983)].

3. Relativistic formulation of NMR shielding tensor

In the presence of an external uniform magnetic field $\vec{B}_0$, the electronic non-relativistic Hamiltonian is given by:

$$\mathcal{H} = \sum_{i=1}^{n} \left[\frac{1}{2} \vec{p}_i^{\,2} + V(i) + \sum_{i<j}^{n} \frac{1}{r_{ij}} \right], \quad (14)$$

where the electronic impulsion $\vec{p}_j$ is given by:

$$\vec{p}_i = \left[-i \vec{\nabla}_i + e \vec{A}_i \right] \qquad \text{where} \qquad \vec{A}_i = \frac{1}{2} \left(\vec{B}_0 \wedge \vec{r}_{i0} \right) + \frac{\mu_0}{4\pi} \sum_N \frac{\vec{\mu}_N \wedge \vec{r}_{iN}}{r_{iN}^3}, \quad (15)$$

where $\vec{A}_i$ stands for the vector potential induced by the nuclear moments $\vec{\mu}_N$ and the external uniform magnetic field $\vec{B}_0$. μ_0 stands for dielectric permittivity. r_{ij} is the modulus of the vector $\vec{r}_{ij}$ separating the electrons i and j. $\vec{r}_{iN}$ is the vector separating the electron i and the nuclei N.

The relativistic effects are important for the fourth and fifth rows in the periodic table and for transitions metals [Pyykkö (1988)]. In terms of perturbations with respect to $\mu_{N,\alpha}$ and $B_{0,\beta}$ where α and β stand for cartesian coordinates ($\alpha, \beta \in (x,y,z)$), the electronic relativistic Hamiltonian is given by:

$$\mathcal{H} = \mathcal{H}^{(0)} + \mathcal{H}^{(r)} + \mu_{N,\alpha} \mathcal{H}_\alpha^{(0,1)} + B_{0,\beta} \mathcal{H}_\beta^{(1,0)} + \mu_{N,\alpha} B_{0,\beta} \mathcal{H}_{\alpha\beta}^{(1,1)} + \cdots, \quad (16)$$

where $\mathcal{H}^{(0)}$ is the zeroth-order hamiltonian (1) and $\mathcal{H}^{(r)}$ is the relativistic perturbation term, which is independent of the magnetic perturbations and is given by [Fukui & Baba (1998)]:

$$\mathcal{H}^{(r)} = \sum_{j<k}^{n} \left[\mathcal{H}_{1,j}^{(r)} + \mathcal{H}_{2,j}^{(r)} + \mathcal{H}_{3,j}^{(r)} + \mathcal{H}_{4,j}^{(r)} + \mathcal{H}_{5,j}^{(r)} \right], \tag{17}$$

which include the contributions; $\mathcal{H}_{1,j}^{(r)}$: two-electron Darwin term, $\mathcal{H}_{2,j}^{(r)}$: two-electron spin-orbit term, $\mathcal{H}_{3,j}^{(r)}$: the retarded orbit-orbit term, $\mathcal{H}_{4,j}^{(r)}$: spin-other-orbit term and $\mathcal{H}_{5,j}^{(r)}$: spin-spin term.

The perturbations $\mathcal{H}_{\alpha}^{(0,1)} = \left(\frac{\partial \mathcal{H}}{\partial \mu_{N,\alpha}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}}$, $\mathcal{H}_{\beta}^{(1,0)} = \left(\frac{\partial \mathcal{H}}{\partial B_{0,\beta}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}}$ and $\mathcal{H}_{\alpha\beta}^{(1,1)} = \left(\frac{\partial^2 \mathcal{H}}{\partial \mu_{N,\alpha}\partial B_{0,\beta}}\right)_{\{\vec{\mu}_N=\vec{0},\vec{B}_0=\vec{0}\}}$ are given by [Fukui & Baba (1998)]:

$$\mathcal{H}_{\alpha}^{(0,1)} = \frac{\mu_0}{2\,\pi} \sum_{j=1}^{n} \frac{\vec{l}_{jN,\beta}}{r_{jN}^3} + \frac{\mu_0}{4\,\pi} \sum_{j=1}^{n} \left[\frac{8\,\pi}{3} \delta(\vec{r}_{jN}) \sigma_{\beta}(j) - \frac{\sigma_{\beta}(j)}{r_{jN}^3} + 3\, r_{jN,\beta} \frac{\vec{r}_{jN} \cdot \vec{\sigma}(j)}{r_{jN}^5} \right] \tag{18}$$

$$\mathcal{H}_{\beta}^{(1,0)} = \frac{1}{2} \sum_{j=1}^{n} \vec{l}_{j,\beta} + \frac{1}{2} \sum_{j=1}^{n} \sigma_{\beta}(j) \tag{19}$$

$$\mathcal{H}_{\alpha\beta}^{(1,1)} = \frac{\mu_0}{8\pi} \sum_{j=1}^{n} \frac{\vec{r}_j \cdot \vec{r}_{jN} \delta_{\alpha\beta} - r_{jN,\alpha}\, r_{j,\beta}}{r_{jN}^3}, \tag{20}$$

where $\vec{l}_{jX} = -i \left(\vec{r}_{jX} \wedge \vec{\nabla}_j \right)$, $\vec{l}_j = -i \left(\vec{r}_j \wedge \vec{\nabla}_j \right)$ and $\vec{\sigma}_j$ stands for the Pauli spin matrix of the electron j and its cartesian coordinates are given by:

$$\sigma_{j,x} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_{j,y} = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \sigma_{j,z} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

4. Fourier transformation for the analytic development of NMR integrals

The operators involved in equations (18), (19) and (20) lead to very complicated integrals. The analytic development of the these NMR integrals is difficult due to the presence of the operator involving $1/r^n$, which is not the case of the usual three-center molecular integrals (zeroth order molecular integrals) where the Coulomb operator $1/r$ is involved.

In this review, we present the method based on Fourier transform that led to analytic expressions for first and second order integrals of the shielding tensor. Among the operators involved in integrals of the shielding tensors are $\frac{\vec{r}_j \cdot \vec{r}_{jN} \delta_{\alpha\beta} - r_{jN,\alpha}\, r_{j,\beta}}{r_{jN}^3}$ in equation (20) for the second order terms and $3 r_{jN,\beta} \left[\frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} \right]$ in equation (18) in the case of first order relativistic terms.

The integrals induced by the above operators are given by:

$$\mathcal{I}_{13} = \int_{\vec{r}_j} \left[\chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_{jA}) \right]^* \, 3\, r_{jN,\beta} \, \frac{\vec{r}_{jN} \cdot \vec{\sigma}_j}{r_{jN}^5} \, \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB}) \, \mathrm{d}\vec{r}_j, \tag{21}$$

$$\mathcal{I}_{23} = \int_{\vec{r}_j} \left[\chi^{m_1}_{n_1,l_1}(\zeta_1, \vec{r}_{jA})\right]^* \frac{\vec{r}_j \cdot \vec{r}_{jN}\delta_{\alpha\beta} - r_{jN,\alpha}\, r_{j,\beta}}{r^3_{jN}} \chi^{m_2}_{n_2,l_2}(\zeta_2, \vec{r}_{jB})\, \mathrm{d}\vec{r}_j, \tag{22}$$

where $\vec{r}_{jA} = \vec{r}_j - \overrightarrow{OA}$, $\vec{r}_{jB} = \vec{r}_j - \overrightarrow{OB}$ and $\vec{r}_{jN} = \vec{r}_j - \overrightarrow{ON}$. A, B and N are three arbitrary points of the Euclidean space and 0 is the origin of the fixed coordinate system.

4.1 First order integrals

After expanding the operator in the integrals (21), we can write $\mathcal{I}_{13}$ as follows:

$$\mathcal{I}_{13} = -\sum_{\alpha} \sigma_{j,\alpha} \int_{\vec{r}_j} \left[\chi^{m_1}_{n_1,l_1}(\zeta_1, \vec{r}_{jA})\right]^* r_{jN,\beta} \frac{\partial}{\partial r_{jN,\alpha}} \left(\frac{1}{r^3_{jN}}\right) \chi^{m_2}_{n_2,l_2}(\zeta_2, \vec{r}_{jB}) \mathrm{d}\vec{r}_j. \tag{23}$$

Let $\mathcal{I}^{(\alpha,\beta)}_{13}$ represent the integrals in summation of the RHS of the above equation. Using equation (5), the integrals $\mathcal{I}^{(\alpha,\beta)}_{13}$ are expressed as linear combinations of integrals ${}_B\mathcal{I}^{(\alpha,\beta)}_{13}$ over B functions which are given by:

$${}_B\mathcal{I}^{(\alpha,\beta)}_{13} = \int_{\vec{r}_j} \left[B^{m_1}_{n_1,l_1}(\zeta_1, \vec{r}_{jA})\right]^* r_{jN,\beta} \frac{\partial}{\partial r_{jN,\alpha}} \left(\frac{1}{r^3_{jN}}\right) B^{m_2}_{n_2,l_2}(\zeta_2, \vec{r}_{jB}) \mathrm{d}\vec{r}_j. \tag{24}$$

Using the Fourier transform method, we obtain:

$${}_B\mathcal{I}^{(\alpha,\beta)}_{13} = (2\,\pi)^{-3/2} \int_{\vec{k}} \overline{r_{jN,\beta} \frac{\partial}{\partial r_{jN,\alpha}} \left(\frac{1}{r^3_{jN}}\right)} \left[\int_{\vec{r}_j} \left[B^{m_1}_{n_1,l_1}(\zeta_1, \vec{r}_{jA})\right]^* e^{-i\,\vec{k}\cdot\vec{r}_{jN}} B^{m_2}_{n_2,l_2}(\zeta_2, \vec{r}_{jB})\, \mathrm{d}\vec{r}_j\right] \mathrm{d}\vec{k}. \tag{25}$$

In the case where α and β represent two different cartesian coordinates, the Fourier transform of the operator is given by [Safouhi (2010b)]:

$$\overline{r_\beta \frac{\partial}{\partial r_\alpha} \left(\frac{1}{r^3}\right)} = \sqrt{\frac{2}{\pi}} \frac{k_\alpha\, k_\beta}{k^2}. \tag{26}$$

In the case where α and β represent the same cartesian coordinate, the calculations leads to the potential $1/r^3$, which poses serious difficulties because of the singularity and its Fourier transform does not exist in a sense of classical analysis. This case is a part of ongoing research where the theory of generalized functions will be used in order to derive the Fourier transform of the operator in the generalized function sense.

Using the analytic expression (11) obtained by Trivedi and Steinborn [Trivedi & Steinborn (1983)] for the integrals over $\vec{r}_j$ involved in equation (25) and with the help of equation (26), one can derive the following analytic expression for the integrals ${}_B\mathcal{I}^{(\alpha,\beta)}_{13}$ [Safouhi (2010b)]:

$$\begin{aligned} {}_B\mathcal{I}^{(\alpha,\beta)}_{13} = {} & \frac{4^3\,\pi\,(2l_1+1)!!\,(2l_2+1)!!\,(n_1+l_1+n_2+l_2+1)!\,\zeta_1^{2n_1+l_1-1}\,\zeta_2^{2n_2+l_2-1}}{(n_1+l_1)!\,(n_2+l_2)!\,2^{n_1+n_2+l_1+l_2+2}} \\ & \times \sum_{l'_1=0}^{l_1} (-i)^{l_1+l'_1} \sum_{m'_1=-l'_1}^{l'_1} \frac{\left\langle l_1 m_1 \left| l'_1 m'_1 \right| l_1 - l'_1 m_1 - m'_1 \right\rangle}{(2l'_1+1)!![2(l_1-l'_1)+1]!!} \end{aligned}$$

$$
\begin{aligned}
&\times \sum_{l_2'=0}^{l_2} (-i)^{l_2+l_2'} \sum_{m_2'=-l_2'}^{l_2'} \frac{\langle l_2 m_2 \left| l_2' m_2' \right| l_2 - l_2' m_2 - m_2' \rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!} \\
&\times \sum_{l'=l'_{\min},2}^{l_1'+l_2'} (-1)^{l_1'} \left\langle l_2' m_2' \left| l_1' m_1' \right| l' m_2' - m_1' \right\rangle \; R_2^{l'} \, Y_{l'}^{m_2'-m_1'}(\theta_{\vec{R}_2}, \varphi_{\vec{R}_2}) \\
&\times \sum_{l_{12}=l_{12min},2}^{l_1-l_1'+l_2-l_2'} \left\langle l_2 - l_2' m_2 - m_2' \left| l_1 - l_1' m_1 - m_1' \right| l_{12} m_{12} \right\rangle \\
&\times \sum_{m_3=-1}^{1} \sum_{m_4=-1}^{1} (-1)^{m_4} \, c_{\alpha,m_3} \, c_{\beta,m_4} \sum_{l''=l''_{\min,2}}^{2} \left\langle 1\, m_4 | 1\, m_3 | l''\, m_4 - m_3 \right\rangle \\
&\times \sum_{\lambda=\lambda_{\min,2}}^{l''+l_{12}} (-i)^{\lambda} \; < l_{12} m_{12} | l'' m_3 - m_4 | \lambda \, \mu > \\
&\times \sum_{j=0}^{\Delta l} \frac{(-2)^j \, \binom{\Delta l}{j}}{(n_1+n_2+l_1+l_2-j+1)!} \\
&\times \int_{s=0}^{1} s^{n_{22}} (1-s)^{n_{11}} \, Y_{\lambda}^{\mu}(\theta_{\vec{v}}, \varphi_{\vec{v}}) \\
&\times \left[\int_{x=0}^{+\infty} x^{n_x} \; \frac{\hat{k}_{\nu}\left[R_2 \, \gamma(s,x)\right]}{[\gamma(s,x)]^{n_\gamma}} \, j_{\lambda}(v\, x) \, \mathrm{d}x \right] \mathrm{d}s,
\end{aligned}
\tag{27}
$$

where:

$$
\begin{aligned}
&\vec{R}_1 \;=\; \overrightarrow{AN}, \vec{R}_2 \;=\; \overrightarrow{AB} \quad \text{and} \quad \vec{v} \;=\; (1-s)\,\vec{R}_2 - \vec{R}_1 \\
&\gamma(s,x) \;=\; \sqrt{(1-s)\,\zeta_1^2 + s\,\zeta_2^2 + s\,(1-s)\,x^2} \\
&n_\gamma = 2(n_1+n_2+l_1+l_2) - (l_1'+l_2'+l') + 1 \\
&n_{11} = n_1 + l_1 + l_2 - l_2', \, n_{22} = n_2 + l_2 + l_1 - l_1' \\
&\nu = n_1 + n_2 + l_1 + l_2 - l' - j + \tfrac{1}{2} \\
&m_{12} = (m_2 - m_2') - (m_1 - m_1') \\
&n_k = l_1 - l_1' + l_2 - l_2' + 2 \\
&\mu = m_{12} - m_3 + m_4 \\
&\Delta l = \tfrac{l_1'+l_2'-l'}{2}.
\end{aligned}
\tag{28}
$$

In the case of one- and two-center integrals ${}_B\mathcal{I}_{11}^{(\alpha,\beta)}$ and ${}_B\mathcal{I}_{12}^{(\alpha,\beta)}$, corresponding to $A = B = N$ and $A = B \neq N$ respectively, we derived analytical expressions in [Slevinsky et al. (2010)].

For the one-center integrals ($A = B = N$):

$$
\begin{aligned}
{}_B\mathcal{I}_{11}^{(\alpha,\beta)} \;=\; & -\frac{\zeta_1^{l_1} \, \zeta_2^{l_2} \, \zeta_s^{2-l_1-l_2}}{\sqrt{\pi}\, 2^{2\,n_1+l_1+2\,n_2+l_2+3}\,(n_1+l_1)!\,(n_2+l_2)!} \\
& \times \sum_{m_3=-1}^{1} \sum_{m_4=-1}^{1} (-1)^{m_3} \, c_{\alpha,m_3} \, c_{\beta,m_4}
\end{aligned}
$$

$$\times \sum_{l=l_{\min},2}^{2} 2^{-l}\ \langle 1\, m_4 | 1\, m_3 | l\, m_4 - m_3 \rangle\ \langle l_1 m_1 | l_2 m_2 | l m_1 - m_2 \rangle\ \delta_{m_1 - m_2, m_4 - m_3}$$

$$\times \sum_{\tau=2}^{n_1+n_2} \sum_{\varsigma=\tau_1}^{\tau_2} \frac{2^{\tau}\, \zeta_1^{\varsigma-1}\, \zeta_2^{\tau-\varsigma-1}}{\zeta_s^{\tau}} \frac{(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,(\tau+l_1+l_2)_{l+1}}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma(l+\frac{3}{2})}$$

$$\times \sum_{r=0}^{\eta'} \frac{(\frac{\eta}{2})_r\, (\frac{\eta+1}{2})_r\, (-r-\frac{l+1}{2})_{l_1+l_2+\tau-1}}{(l+\frac{3}{2})_r\, r!}, \tag{29}$$

where:

$$\begin{aligned} \tau_1 &= \max(1, \tau - n_2) \\ \tau_2 &= \min(n_1, \tau - 1) \\ \zeta_s &= \zeta_1 + \zeta_2 \\ \eta &= l - \tau - l_1 - l_2 + 1 \\ \eta' &= -\tfrac{\eta}{2} \quad \text{if} \quad \eta \quad \text{is even otherwise} \quad \eta' = -\tfrac{\eta+1}{2}. \end{aligned} \tag{30}$$

For the two-center integrals ($A = B \neq N$):

$${}_B\mathcal{I}_{12}^{(\alpha,\beta)} = \frac{\sqrt{\pi}\, \zeta_1^{l_1}\, \zeta_2^{l_2}\, \zeta_s^{l_1+l_2-1}\, R^{2l_1+2l_2-3}}{4^{n_1+l_1+n_2+l_2}\,(n_1+l_1)!\,(n_2+l_2)!} \sum_{l=l_{min},2}^{l_1+l_2} 2^{-l}\ \langle l_1 m_1 | l_2 m_2 | l m_1 - m_2 \rangle$$

$$\times \sum_{m_3=-1}^{1} \sum_{m_4=-1}^{1} (-1)^{m_3}\, c_{\alpha,m_3}\, c_{\beta,m_4} \sum_{l'=l'_{\min,2}}^{2} \left\langle 1\, m_4 | 1\, m_3 | l'\, m_4 - m_3 \right\rangle$$

$$\times \sum_{\lambda=\lambda_{\min,2}}^{l+l'} (R\,\zeta_s)^{-\lambda}\ \left\langle l' m_4 - m_3 | l m_1 - m_2 | \lambda m_4 - m_3 - m_1 + m_2 \right\rangle Y_{\lambda}^{m_4-m_3-m_1+m_2}(\theta_{\vec{R}}, \varphi_{\vec{R}})$$

$$\times \sum_{\tau=2}^{n_1+n_2} \sum_{\varsigma=\tau_1}^{\tau_2} \frac{R^{2\tau}\,(2n_1-\varsigma-1)!\,(2n_2-\tau+\varsigma-1)!\,\zeta_1^{\varsigma-1}\zeta_2^{\tau-\varsigma-1}\zeta_s^{\tau}\,(\tau+l_1+l_2)_{l+1}}{(\varsigma-1)!\,(n_1-\varsigma)!\,(\tau-\varsigma-1)!\,(n_2-\tau+\varsigma)!\,\Gamma(l+\frac{3}{2})}$$

$$\times \sum_{r=0}^{\eta'} \frac{(\frac{\eta}{2})_r\,(\frac{\eta+1}{2})_r}{(l+\frac{3}{2})_r\, r!} \sum_{s=0}^{r+\frac{l-\lambda}{2}} \binom{r+\frac{l-\lambda}{2}}{s} \frac{2^s\,(1-l_1-l_2-\tau)_s}{(R\,\zeta_s)^{2s}}\, \hat{k}_{\lambda-l_1-l_2-\tau+s+\frac{3}{2}}(R\,\zeta_s). \tag{31}$$

4.2 Second order integrals

The second order integrals $\mathcal{I}_{23}$ are given by (22). For simplicity and without loss of generality, we assume $A = O$ in equation (25).

The operator involved in (22) is given by:

$$\frac{\vec{r}_j \cdot \vec{r}_{jN}\delta_{\alpha\beta} - r_{jN,\alpha}\, r_{j,\beta}}{r_{jN}^3} = \begin{cases} \dfrac{-r_{jN,\alpha}\, r_{j,\beta}}{r_{jN}^3} & \text{when } \alpha \neq \beta \\ \dfrac{r_{jN,u}\, r_{j,u}}{r_{jN}^3} + \dfrac{r_{jN,v}\, r_{j,v}}{r_{jN}^3} & \text{when } \alpha = \beta \quad \text{and} \quad u, v \neq \alpha \in \{x, y, z\}. \end{cases} \tag{32}$$

From the above equation, it is obvious that the integrals $\mathcal{I}_{23}$ can be expressed in terms of integrals of the form:

$$\mathcal{I}_{23}^{\alpha\beta} = \int_{\vec{r}_j} \left[\chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_j)\right]^*\ \frac{r_{jN,\alpha}\, r_{j,\beta}}{r_{jN}^3}\ \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB})\, \mathrm{d}\vec{r}_j. \tag{33}$$

The cartesian coordinate $r_{jN,\alpha}$ and $r_{j,\beta}$ can be expressed in terms of spherical harmonics and r_{jN} and r_j respectively as follows:

$$r_{jN,\alpha} = r_{jN} \sum_{\mu_1=-1}^{1} c_{\alpha,\mu_1} Y_1^{\mu_1}(\theta_{\vec{r}_{jN}}, \phi_{\vec{r}_{jN}}) \quad \text{and} \quad r_{j,\beta} = r_j \sum_{\mu_2=-1}^{1} c_{\beta,\mu_2} Y_1^{\mu_2}(\theta_{\vec{r}_j}, \phi_{\vec{r}_j}), \tag{34}$$

where the coefficients $c_{\alpha,\mu}$ are given as follows:

$$\begin{cases} c_{x,-1} = \sqrt{\frac{2\pi}{3}}, & c_{y,-1} = i\sqrt{\frac{2\pi}{3}} & \text{and } c_{z,-1} = 0 \\ c_{x,0} = 0, & c_{y,0} = 0 & \text{and } c_{z,0} = \sqrt{\frac{4\pi}{3}} \\ c_{x,1} = -\sqrt{\frac{2\pi}{3}}, & c_{y,1} = i\sqrt{\frac{2\pi}{3}} & \text{and } c_{z,1} = 0. \end{cases} \tag{35}$$

Using the analytic expression of the Unormalized STFs (2), one can obtain:

$$\begin{aligned} r_{j,\beta} \left[\chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_j)\right]^* &= \left[r_j \sum_{\mu_2=-1}^{1} c_{\beta,\mu_2} Y_1^{\mu_2}(\theta_{\vec{r}_j}, \phi_{\vec{r}_j})\right] r_j^{n_1-1} \, \mathrm{e}^{-\zeta_1 r_j} \left[Y_{l_1}^{m_1}(\theta_{\vec{r}_j}, \varphi_{\vec{r}_j})\right]^* \\ &= \sum_{\mu_2=-1}^{1} c_{\beta,\mu_2} \, r_j^{n_1} \, \mathrm{e}^{-\zeta_1 r_j} \left[Y_{l_1}^{m_1}(\theta_{\vec{r}_j}, \varphi_{\vec{r}_j})\right]^* Y_1^{\mu_2}(\theta_{\vec{r}_j}, \phi_{\vec{r}_j}). \end{aligned} \tag{36}$$

The product of two spherical harmonics can be linearized by Gaunt coefficients as follows:

$$\left[Y_{l_1}^{m_1}(\theta, \varphi)\right]^* Y_{l_2}^{m_2}(\theta, \varphi) = \sum_{l=l_{\min},2}^{l_1+l_2} \langle l_2 \, m_2 | l_1 \, m_1 | l \, m_2 - m_1 \rangle \, Y_l^{m_2-m_1}(\theta, \varphi), \tag{37}$$

where the summation index l runs in steps of 2 from $l_{\min}$ to $l_1 + l_2$. The constant $l_{\min}$ is given by [Weniger & Steinborn (1982)]:

$$l_{\min} = \begin{cases} \max(|l_1 - l_2|, |m_2 - m_1|) & \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \text{ is even} \\ \max(|l_1 - l_2|, |m_2 - m_1|) + 1 & \text{if } l_1 + l_2 + \max(|l_1 - l_2|, |m_2 - m_1|) \text{ is odd.} \end{cases} \tag{38}$$

From equation (37), it follows that:

$$\begin{aligned} r_{j,\beta} \left[\chi_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}_j)\right]^* &= \sum_{\mu_2=-1}^{1} c_{\beta,\mu_2} \, r_j^n \, \mathrm{e}^{-\zeta r_j} \sum_{l=l_{\min},2}^{l_1+1} \langle 1 \, \mu_2 | l_1 \, m_1 | l \, \mu_2 - m_1 \rangle \, Y_l^{\mu_2-m_1}(\theta_{\vec{r}_j}, \varphi_{\vec{r}_j}) \\ &= \sum_{\mu_2=-1}^{1} \sum_{l=l_{\min},2}^{l_1+1} c_{\beta,\mu_2} \, \langle 1 \, \mu_2 | l_1 \, m_1 | l \, \mu_2 - m_1 \rangle \, (-1)^{\mu_2-m_1} \left[\chi_{n_1+1,l}^{m_1-\mu_2}(\zeta_1, \vec{r}_j)\right]^*. \end{aligned} \tag{39}$$

Using equations (34) and (39), we obtain the following relation:

$$\begin{aligned} \mathcal{I}_{23}^{\alpha\beta} = &\sum_{\mu_2=-1}^{1} \sum_{l=l_{\min},2}^{l_1+1} \sum_{\mu_1=-1}^{1} (-1)^{\mu_2-m_1} \, c_{\beta,\mu_2} \, c_{\alpha,\mu_1} \, \langle 1 \, \mu_2 | l_1 \, m_1 | l \, \mu_2 - m_1 \rangle \\ &\times \int_{\vec{r}_j} \left[\chi_{n_1+1,l}^{m_1-\mu_2}(\zeta_1, \vec{r}_j)\right]^* \frac{Y_1^{\mu_1}(\theta_{\vec{r}_{jN}}, \phi_{\vec{r}_{jN}})}{r_{jN}^2} \, \chi_{n_2,l_2}^{m_2}(\zeta_2, \vec{r}_{jB}) \, \mathrm{d}\vec{r}_j. \end{aligned} \tag{40}$$

Let $\tilde{\mathcal{I}}_{23}^{\alpha\beta}$ represent the integrals involved in the above equation. Using equation (5), these integrals can be expressed as linear combinations of integrals ${}_B\hat{\mathcal{I}}_{23}^{\alpha\beta}$ over B functions of the form:

$$ {}_B\hat{\mathcal{I}}_{23}^{\alpha\beta} = \int_{\vec{r}_j} \left[B_{\tilde{n}_1,l}^{\tilde{m}_1}(\zeta_1,\vec{r}_j) \right]^* \frac{Y_1^{\mu_1}(\theta_{\vec{r}_{jN}},\phi_{\vec{r}_{jN}})}{r_{jN}^2} B_{n_2,l_2}^{m_2}(\zeta_2,\vec{r}_{jB})\,\mathrm{d}\vec{r}_j, \tag{41} $$

where $\tilde{m}_1 = m_1 - \mu_2$ and $\tilde{n}_1 = n_1 + 1$.

Using the Fourier transform method, we obtain:

$$ {}_B\hat{\mathcal{I}}_{23}^{\alpha\beta} = (2\,\pi)^{-3/2} \int_{\vec{k}} \overline{\frac{Y_1^{\mu_1}(\theta_{\vec{r}_{jN}},\phi_{\vec{r}_{jN}})}{r_{jN}^2}} \left[\int_{\vec{r}_j} \left[B_{\tilde{n}_1,l}^{\tilde{m}_1}(\zeta_1,\vec{r}_j) \right]^* e^{-i\,\vec{k}\cdot\vec{r}_{jN}} B_{n_2,l_2}^{m_2}(\zeta_2,\vec{r}_{jB})\,\mathrm{d}\vec{r}_j \right] \mathrm{d}\vec{k}. \tag{42} $$

The Fourier transform of the operator involved in the above integrals is given by [Berlu & Safouhi (2008)]:

$$ \overline{\left(\frac{Y_1^{\mu}(\theta_{\vec{r}_{jN}},\phi_{\vec{r}_{jN}})}{r_{jN}^2} \right)}(\vec{k}) = -i\,\sqrt{\frac{2}{\pi}}\,\frac{Y_1^{\mu}(\theta_{\vec{k}},\phi_{\vec{k}})}{k}. \tag{43} $$

Using the analytic expression (11) obtained by Trivedi and Steinborn [Trivedi & Steinborn (1983)] for the integrals over $\vec{r}_j$ involved in equation (42) and equation (43), one can derive the following analytic expression for the integrals ${}_B\hat{\mathcal{I}}_{23}^{\alpha\beta}$ [Berlu & Safouhi (2008)]:

$$ \begin{aligned} {}_B\hat{\mathcal{I}}_{23}^{\alpha\beta} &= 8\,(4\pi)^2\,(2l_1+1)!!\,(2l_2+1)!!\,\frac{(\tilde{n}_1+n_2+l_1+l_2+1)!}{(\tilde{n}_1+l_1)!\,(n_2+l_2)!}\,\frac{\zeta_1^{2\tilde{n}_1+l_1-1}\,\zeta_2^{2n_2+l_2-1}}{2^{\tilde{n}_1+n_2+l_1+l_2+1}} \\ &\times \sum_{l_1'=0}^{l_1} \sum_{m_1'=-l_1'}^{l_1'} (-i)^{l_1+l_1'} \frac{\langle l_1,\,\tilde{m}_1\,|l_1',\,m_1'|\,l_1-l_1',\,\tilde{m}_1-m_1'\rangle}{(2l_1'+1)!![2(l_1-l_1')+1]!!} \\ &\times \sum_{l_2'=0}^{l_2} \sum_{m_2'=-l_2'}^{l_2'} (-i)^{l_2+l_2'} \frac{\langle l_2,\,m_2\,|l_2',\,m_2'|\,l_2-l_2',\,m_2-m_2'\rangle}{(2l_2'+1)!![2(l_2-l_2')+1]!!} \\ &\times \sum_{l'=l'_{\min},2}^{l_1'+l_2'} (-1)^{l_1'}\,\langle l_2',\,m_2'\,|l_1',\,m_1'|\,l'm_2',\,-m_1'\rangle\,R_2^{l'}\,Y_{l'}^{m_2'-m_1'}\left(\theta_{\overrightarrow{OB}},\varphi_{\overrightarrow{OB}}\right) \\ &\times \sum_{l_{12}=l_{12\,\min},2}^{l_1-l_1'+l_2-l_2'} \langle l_2-l_2',\,m_2-m_2'\,|l_1-l_1',\,\tilde{m}_1-m_1'|\,l_{12},\,m_{12}\rangle \\ &\times \sum_{\lambda=\lambda_{\min},2}^{1+l_{12}} (-i)^{\lambda+1}\,\langle\lambda,\,\mu\,|l_{12},\,m_{12}|\,1,\,\mu_1\rangle \\ &\times \sum_{j=0}^{\Delta l} \binom{\Delta l}{j} \frac{(-2)^j}{(\tilde{n}_1+n_2+l_1+l_2-j+1)!} \\ &\times \int_{s=0}^{1} s^{n_2+l_2+l_1-l_1'}(1-s)^{\tilde{n}_1+l_1+l_2-l_2'} Y_{\lambda}^{\mu}(\theta_{\overrightarrow{v}},\varphi_{\overrightarrow{v}}) \\ &\times \left[\int_{x=0}^{+\infty} x^{n_x} \frac{\hat{k}_{\nu}[\gamma(s,x)\,R_2]}{\gamma(s,x)^{n_\gamma}}\,j_{\lambda}(vx)\,\mathrm{d}x \right] \mathrm{d}s, \end{aligned} \tag{44} $$

where:

$$
\begin{aligned}
& m_{12} = (m_2 - m_2') - (\tilde{m}_1 - m_1') \text{ and } \mu = \mu_1 + m_{12} \\
& n_\gamma = 2(\tilde{n}_1 + n_2 + l_1 + l_2) - (l_1' + l_2' + l') + 1 \\
& \gamma(s,x) = \sqrt{s\zeta_2^2 + (1-s)\zeta_1^2 + s(1-s)x^2} \\
& \overrightarrow{v} = (1-s)\,\overrightarrow{OB} - \overrightarrow{ON} \quad \text{and} \quad \text{and } v = |\vec{v}| \\
& \nu = \tilde{n}_1 + n_2 + l_1 + l_2 - l' - j + \frac{1}{2} \\
& n_x = l_1 - l_1' + l_2 - l_2' + 1 \\
& \Delta l = (l_1' + l_2' - l')/2.
\end{aligned}
\tag{45}
$$

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	${}_B\mathcal{I}_2^{(x,y)}$
2	1	-1	2.0	2	1	-1	1.5	.844938515752529(-3)
2	1	0	2.0	2	1	0	1.5	.197895122059999(-3)
3	2	-1	2.0	2	1	-1	1.5	-.183961338177373(-4)
3	2	1	2.0	3	2	1	1.5	.314124180426832(-4)
3	2	2	2.0	3	2	2	1.5	.132485365811557(-3)
4	2	1	2.0	2	1	1	1.5	-.361569492726092(-4)
4	2	1	2.0	3	2	1	1.5	.764186724377223(-4)
4	2	2	2.0	3	2	2	1.5	.331525812542680(-3)
4	2	0	2.0	4	2	0	1.5	-.297315128733290(-4)
4	2	1	2.0	4	2	1	1.5	.215564810358993(-3)
4	2	2	2.0	4	2	2	1.5	.951453780055960(-3)

Table 1. Evaluation of ${}_B\mathcal{I}_1^{(x,y)}$ (29).

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	${}_B\mathcal{I}_2^{(y,z)}$
2	1	1	1.0	2	1	-1	1.5	-.980852389239356(-3)
3	2	1	1.0	2	1	-1	1.5	-.319537014904337(-1)
3	2	1	1.0	2	1	1	1.5	.858668805557491(-2)
3	2	1	1.0	3	2	-1	1.5	-.219369423462985(-1)
3	2	2	1.0	3	2	-2	1.5	.391684472826858(-4)
3	2	2	1.0	3	2	-1	1.5	-.204743121872522(-1)
3	2	2	1.0	3	2	1	1.5	.163009587528461(2)
4	2	1	1.0	2	1	-1	1.5	-.414819029773496(-1)
4	2	2	1.0	3	2	-2	1.5	.441086792217064(-4)
4	2	2	1.0	3	2	-1	1.5	-.298416140021138(-1)
4	2	2	1.0	3	2	1	1.5	.291083584089616(2)

Table 2. Evaluation of ${}_B\mathcal{I}_2^{(y,z)}$ (31). $\vec{R} = (1.5, 75^o, 0^o)$ in spherical coordinates.

n_1	l_1	m_1	ζ_1	n_2	l_2	m_2	ζ_2	${}_B\mathcal{I}_3^{(x,z)}$
2	1	-1	2.0	2	1	1	1.0	.769304745002408(-4)
2	1	1	2.0	2	1	1	1.0	-.620498371396534(-4)
3	2	1	2.0	2	1	0	1.0	-.146444907098019(-5)
3	2	1	2.0	2	1	1	1.0	-.576608712417475(-5)
3	2	1	2.0	3	2	1	1.0	.137450124735083(-6)
3	2	1	2.0	3	2	-1	1.0	-.117106174581176(-6)
3	2	2	2.0	3	2	-2	1.0	.287818321676003(-6)
3	2	2	2.0	3	2	1	1.0	.143900856736229(-6)
3	2	2	2.0	3	2	2	1.0	-.121032718682770(-5)
4	2	-1	2.0	3	2	1	1.0	-.359169492307861(-6)
4	2	1	2.0	3	2	1	1.0	.343245699707943(-6)

Table 3. Evaluation of $\mathcal{I}_3^{(x,z)}$ (27). $\vec{R}_1 = (12.0, 90^o, 0^o)$ and $\vec{R}_2 = (2.0, 90^o, 0^o)$ in spherical coordinates.

5. Conclusion

In the present review, we showed how the Fourier transformation method allowed the derivation of compact formulae for one of the most challenging integrals, namely molecular multi-center integrals and NMR multi-center integrals.

Analytic expressions are obtained for integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor as well as integrals of second order in the non-relativistic calculation of the shielding tensor. The basis set of ETFs is used and it is well known that these functions are better suited than GTFs.

The obtained analytic expressions for the one- and two-center integrals can be computed easily and no quadrature rule is required. In the case of the three-center integrals, we need to compute semi-infinite integrals involving oscillatory functions. These oscillatory integrals can be computed to a high pre-determined accuracy using existing methods and algorithms based on extrapolation methods and numerical quadrature [Berlu & Safouhi (2003); Duret & Safouhi (2007); Safouhi (2001b; 2004; 2010a); Slevinsky & Safouhi (2009)].

Numerical tables for the NMR integrals of interest can be found in [Safouhi (2010b); Slevinsky et al. (2010)].

6. Acknowledgment

The author acknowledges the financial support for this research by the Natural Sciences and Engineering Research Council of Canada (NSERC).

7. References

Agmon, S. (1985). *Bounds on exponential decay of eigenfunctions of Schrödinger operators, in S. Graffi (editor), Schrödinger operators*, Springer-Verlag, Berlin.

Barnett, M. (1990). Molecular integrals over Slater orbitals, *Chem. Phys. Lett.* 166: 65–70.

Berlu, L. & Safouhi, H. (2003). An extremely efficient and rapid algorithm for a numerical evaluation of three-center nuclear attraction integrals over Slater type functions, *J. Phys. A: Math. Gen.* 36: 11791–11805.

Berlu, L. & Safouhi, H. (2008). Analytical treatment of nuclear magnetic shielding tensor integrals over exponential type functions, *J. Theor. Comp. Chem.* 7: 1215–1225.

Boys, S. (1950a). Electronic Wave Functions. I. A General Method of Calculation for the Stationary States of Any Molecular System , *Proc. R. Soc. Lond. Series A, Math. & Phys. Sciences.* 200: 542–554.

Boys, S. (1950b). Electronic Wave Functions. II. A Calculation for the Ground State of the Beryllium Atom, *Proc. R. Soc. Lond. Series A, Math. & Phys. Sciences.* 201: 125–137.

Condon, E. & Shortley, G. (1951). *The theory of atomic spectra*, Cambridge University Press, Cambridge, England.

Dickson, R. & Ziegler, T. (1996). NMR spin-spin coupling constants from density functional theory with Slater-type basis functions, *J. Phys. Chem.* 100: 5286–5290.

Ditchfield, R. (1974). Self-consistent perturbation-theory of diamagnetism. I. Gauge-invariant LCAO method for NMR chemical-shifts, *Molecular Physics* 27: 789–807.

Duret, S. & Safouhi, H. (2007). The W algorithm and the $\bar{D}$ transformation for the numerical evaluation of three-center nuclear attraction integrals, *Int. J. Quantum Chem.* 107: 1060–1066.

Fernández, J., López, R., Aguado, A., Ema, I. & Ramírez, G. (2001). SMILES Slater Molecular Integrals for Large Electronic Systems: New Program for Molecular Calculations with Slater Type Orbitals, *Int. J. Quant. Chem.* 81: 148–153.

Filter, E. & Steinborn, E. (1978a). Extremely compact formulas for molecular one-electron integrals and Coulomb integrals over Slater-type orbitals, *Phys. Rev. A.* 18: 1–11.

Filter, E. & Steinborn, E. (1978b). The three-dimensional convolution of reduced Bessel functions of physical interest, *J. Math. Phys.* 19: 79–84.

Fukui, H. & Baba, T. (1998). Calculation of nuclear magnetic shieldings XII. Relativistic no-pair equation, *J. Chem. Phys.* 108: 3854–3862.

Fukui, H., Baba, T., Shiraishi, Y., Imanishi, S., Kudo, K., Mori, K. & Shimoji, M. (2004). Calculation of nuclear magnetic shieldings: infinite-order Foldy-Wouthuysen transformation, *Mol. Phys.* 102: 641–648.

Gaunt, J. (1929). The triplets of helium, *Phil. Trans. Roy. Soc.* A. 228: 151–196.

Geller, M. (1962). Two-center, nonintegral, Slater-orbital calculations: Integral formulation and application to the Hydrogen molecule-ion, *J. Chem. Phys.* 36: 2424–2428.

Grotendorst, J. & Steinborn, E. (1988). Numerical evaluation of molecular one- and two-electron multicenter integrals with exponential-type orbitals via the Fourier-transform method, *Phys. Rev. A.* 38: 3857–3876.

Helgaker, T., Jaszuński, M. & Ruud, K. (1999). Ab initio methods for the calculation of NMR shielding and indirect spin-spin coupling constants, *Chem. Rev.* 99: 293–352.

Homeier, H. & Steinborn, E. (1993). Programs for the evaluation of nuclear attraction integrals with B functions, *Comput. Phys. Commun.* 77: 135–151.

Ishida, K. (2003). Molecular integrals over the gauge-including atomic orbitals. II. The Breit-Pauli interaction, *J. Comput. Chem.* 24: 1874–1890.

Kato, T. (1957). On the eigenfunctions of many-particle systems in quantum mechanics, *Commun. Pure Appl. Math.* 10: 151–177.

Kutzelnigg, W. (1988). Present and futur trends in quantum chemical calculations, *J. Mol. Struc (THEOCHEM)* 50: 33–54.

London, F. (1937). The quantic theory of inter-atomic currents in aromatic combinations, *Journal de Physique et le Radium* 8: 397–409.

Niehaus, T., López, R. & Rico, J. (2008). Efficient evaluation of the Fourier transform over products of Slater-type orbitals on different centers, *J. Phys. A: Math. Theor.* 41: 485205–485219.

Niukkanen, A. (1984). Fourier transforms of atomic orbitals. I. Reduction to fourdimensional harmonics and quadratic transformations, *Int. J. Quantum Chem.* 25: 941–955.

Ozdogan, T. & (Editors), M. R. (2008). *Recent Advances in Computational Chemistry. Molecular Integrals over Slater Orbitals*, Published by Transworld Research Network., Kerala, India.

Pople, J., McIver Jr, J. & Ostlund, N. (1968). Self-consistent perturbation theory II. Nuclear spin coupling constants, *J. Chem. Phys.* 49: 2960–2965.

Prosser, F. & Blanchard, C. (1962). On the evaluation of two-center integrals, *J. Chem. Phys.* 36: 1112–1112.

Pyykkö, P. (1988). Relativistic effects in structural chemistry, *Chem. Rev.* 88: 563–594.

Rico, F., López, R., Aguado, A., Ema, I. & Ramírez, G. (1998). Reference program for molecular calculations with Slater-type orbitals, *Int. J. Quantum Chem.* 19: 1284–1293.

Rico, J., Fernández, J., Ema, I., López, R. & Ramírez, G. (1999). Master formulas for two- amd three-center one electron integrals involving cartesian GTO, STO, and BTO, *Int. J. Quantum Chem.* 78: 83–93.

Rico, J., Fernández, J., Ema, I., López, R. & Ramírez, G. (2001). Four-center integrals for gaussian and exponential functions, *Int. J. Quant. Chem.* 81: 16–18.

Safouhi, H. (2001a). An extremely efficient approach for accurate and rapid evaluation of three- center two-electron Coulomb and hybrid integral over *B* functions, *J. Phys. A: Math. Gen.* 34: 881–902.

Safouhi, H. (2001b). The properties of sine, spherical Bessel and reduced Bessel functions for improving convergence of semi-infinite very oscillatory integrals: The evaluation of three-center nuclear attraction integrals over B functions, *J. Phys. A: Math. Gen.* 34: 2801–2818.

Safouhi, H. (2004). Highly accurate numerical results for three-center nuclear attraction and two-electron Coulomb and exchange integrals over Slater type functions, *Int. J. Quantum Chem.* 100: 172–183.

Safouhi, H. (2010a). Bessel, sine and cosine functions and extrapolation methods for computing molecular multi-center integrals, *Numer. Algor.* 54: 141–167.

Safouhi, H. (2010b). Integrals of the paramagnetic contribution in the relativistic calculation of the shielding tensor, *J. Math. Chem.* 48: 601–616.

Schreckenbach, G. & Ziegler, T. (1995). Calculation of NMR shielding tensors using gauge-including atomic orbitals and modern density functional theory, *J. Phys. Chem.* 99: 606–611.

Shavitt, I. (1963). *The Gaussian function in calculation of statistical mechanics and quantum mechanics, Methods in Computational Physics.2. Quantum.Mechanics*, edited by B. Alder, S. Fernbach, M. Rotenberg, Academic Press, New York.

Slater, J. (1932). Analytic atomic wave functions, *Phys. Rev.* 42: 33–43.

Slevinsky, R. & Safouhi, H. (2009). The *S* and *G* transformations for computing three-center nuclear attraction integrals, *Int. J. Quantum Chem.* 109: 1741–1747.

Slevinsky, R., Temga, T., Mouattamid, M. & Safouhi, H. (2010). One- and two-Center ETF-integrals of first order in relativistic calculation of NMR parameters, *J. Phys. A: Math. Theor.* 43: 225202 (14pp).

Steinborn, E. & Filter, E. (1975). Translations of fields represented by spherical-harmonics expansions for molecular calculations. III. Translations of reduced Bessel functions, Slater-type s-orbitals, and other functions, *Theor. Chim. Acta.* 38: 273–281.

Steinborn, E., Homeier, H., Ema, I., López, R. & Ramírez, G. (2000). Molecular calculations with *B* functions, *Int. J. Quantum Chem.* 76: 244–251.

Trivedi, H. & Steinborn, E. (1983). Fourier transform of a two-center product of exponential-type orbitals. Application to one- and two-electron multicenter integrals, *Phys. Rev. A.* 27: 670–679.

Vaara, J. (2007). Theory and computation of nuclear magnetic resonance parameters, *Phys. Chem. Chem. Phys.* 9: 5399–5418.

Watson, M., Handy, N., Cohen, A. & Helgaker, T. (2004). Density-functional generalized-gradient and hybrid calculations of electromagnetic properties using Slater basis sets, *J. Chem. Phys.* 120: 7252–7261.

Weatherford, C. & Jones, H. (1982). *ETO Multicenter Molecular Integrals*, Reidel, Dordrecht.

Weniger, E. (1982). *Reduzierte Bessel-Funktionen als LCAO-Basissatz: Analytische und numerische Untersuchungen, publisher = Ph.D.thesis, Universität Regensburg*.

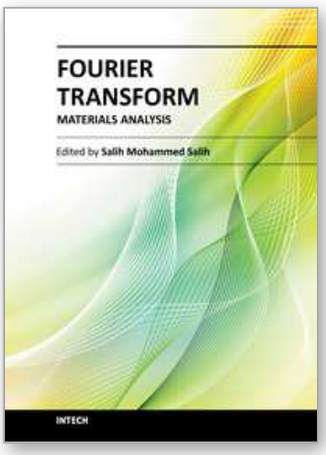
Weniger, E. (1985). Weakly convergent expansions of a plane wave and their use in Fourier integrals, *J. Math. Phys.* 26: 276–291.

Weniger, E. (2005). The spherical tensor gradient operator, *Collect. Czech. Chem. Commun.* 70: 1125–1271.

Weniger, E. & Steinborn, E. (1982). Programs for the coupling of spherical harmonics, *Comput. Phys.Commun.* 25: 149–157.

Weniger, E. & Steinborn, E. (1983a). Numerical properties of the convolution theorems of B functions, *Phys. Rev. A.* 28: 2026–2041.

Weniger, E. & Steinborn, E. (1983b). The Fourier transforms of some exponential-type functions and their relevance to multicenter problems, *J. Chem. Phys.* 78: 6121–6132.



Fourier Transform - Materials Analysis

Edited by Dr Salih Salih

ISBN 978-953-51-0594-7

Hard cover, 260 pages

Publisher InTech

Published online 23, May, 2012

Published in print edition May, 2012

The field of material analysis has seen explosive growth during the past decades. Almost all the textbooks on materials analysis have a section devoted to the Fourier transform theory. For this reason, the book focuses on the material analysis based on Fourier transform theory. The book chapters are related to FTIR and the other methods used for analyzing different types of materials. It is hoped that this book will provide the background, reference and incentive to encourage further research and results in this area as well as provide tools for practical applications. It provides an applications-oriented approach to materials analysis written primarily for physicist, Chemists, Agriculturalists, Electrical Engineers, Mechanical Engineers, Signal Processing Engineers, and the Academic Researchers and for the Graduate Students who will also find it useful as a reference for their research activities.

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

IntechOpen